

Investigation of photo-catalytic activity of $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals using methylene blue dye as test contaminant

Mansi Chitkara · Karamjit Singh · I. S. Sandhu ·
H. S. Bhatti

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Abstract $\text{Zn}_{1-x}\text{Co}_x\text{S}$ ($0.00001 \leq x \leq 0.1$) nanocrystals have been synthesized using facile bottom-up synthesis technique chemical co-precipitation method. Crystallographic and morphological characterizations of synthesized nanomaterials have been done using X-ray diffraction (XRD) and transmission electron microscope (TEM), respectively. XRD studies confirm the formation of zinc blende crystallites having average crystallite size about 3.0 nm, which is in close agreement with the average particle size calculated from TEM micrographs. The photo-catalytic activity potential of synthesized nanocrystals has been tested using methylene blue dye as test contaminant in aqueous media. Photo-catalytic activity dependence on dopant concentration has been described in detail. Moreover, room temperature energy resolved photoluminescence spectra have been also recorded to correlate the various charge carrier recombination and interfacial charge transfer processes.

Keywords Co^{2+} doped ZnS nanocrystals · Methylene blue dye · Photo-catalyst · Energy resolved spectroscopy

Introduction

Since last three decades, a large number of researchers (Becker and Bard 1983; Hauge and Stovngeng 1989; Enders

and Nimtz 1993; Bhargava 1996; Science 1996; Huynh 2002; Singh et al. 2009) throughout globe are trying to explore the potential of semiconductor nanomaterials for next era smart applications. Semiconductor nanomaterials due to their size-tunable photo-physical and photo-chemical properties seem to be good candidates for next era optoelectronic industrial applications (Ranfagni et al. 1993; Bhargava et al. 1994; Reisfeld et al. 2000; Bol et al. 2002; Erwin et al. 2005; Singh 2009) like fast and efficient phosphors, flat panel displays, high-density optical data storage devices, nanosensors, low-threshold quantum dot lasers, size-tunable light emitting diodes (LEDs), nano electro-mechanical systems, biological markers along with efficient photo-catalytic applications (Hoffmann et al. 1995; Anpo and Takeuchi 2003; Chitkara et al. 2010) for environmental cleaning, water purification and H_2 production. Intrinsic and extrinsic semiconductors are usually used as heterogeneous photo-catalysts. Due to their high oxidizing power and non-requirement of oxidizing reagents, heterogeneous photo-catalytic processes are widely utilized to oxidize or mineralize organic/inorganic substances that could not be degraded with biological techniques. Semiconductor photo-catalysts offer the potential for complete elimination of toxic chemicals through their efficiency and potentially broad applicability.

In the present investigation, emphasis has been given to explore the photo-catalytic activity potential of polyvinyl pyrrolidone (PVP) capped bottom-up grown $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals. The photo-catalytic behavior of synthesized nano photo-catalysts have been studied by recording MB dye degradation in aqueous media under UV radiation exposure. As the interfacial charge transfer determines the overall efficiency of the photo-catalyst, energy resolved luminescence spectra have been recorded to examine the competition between charge carrier recombination and

M. Chitkara · I. S. Sandhu
Department of Applied Sciences, Chitkara University,
Rajpura 140 401, Punjab, India

K. Singh (✉) · H. S. Bhatti
Department of Physics, Punjabi University,
Patiala 147 002, Punjab, India
e-mail: dhaliwalkaramjit@gmail.com

charge carrier trapping, followed by the competition between recombination of trapped carriers and interfacial charge transfer.

Experimental

PVP capped $\text{Zn}_{1-x}\text{Co}_x\text{S}$ ($0.00001 \leq x \leq 0.1$) nanocrystals have been synthesized in aqueous media under ambient conditions using chemical co-precipitation method already described by (Singh et al. 2009). Analytical reagent grade chemicals: zinc acetate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$), cobaltous acetate ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$), sodium sulphide ($\text{Na}_2\text{S}_x\text{H}_2\text{O}$), and polyvinyl pyrrolidone (PVP) [$(\text{C}_6\text{H}_9\text{NO})_n$] procured from Hi Media Laboratories Pvt. Ltd. Mumbai (India) and S. D. Fine-Chem Ltd. Mumbai (India) were used without further purification. The aqueous solutions of all the precursors were mixed in stoichiometric concentration under vigorous stirring. In addition, 2 % PVP solution was added to the reaction media to avoid the agglomeration. The resulting precipitates were centrifuged and vacuum dried.

Crystallographic analysis of the synthesized nanomaterials was done using Panalytical's X'Pert Pro Powder X-ray diffractometer. XRD patterns of all the synthesized samples were recorded with $\text{Cu K}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) keeping step size 0.0170° , and step scan time 25.1945s in 2θ range 20° – 60° at generator tension 45 kV and generator current 40 mA. Electron micrographs were recorded using Hitachi (H-7500) TEM operating at 100 kV.

Photo-catalytic activity of the synthesized nanocrystals was examined by monitoring the degradation of MB dye in aqueous media under UV radiation exposure. Dye contaminated aqueous media was prepared by dissolving

3.2349 mg/l MB dye in doubly de-ionized water. Then, 400 mg of nano photo-catalyst was dispersed in dye contaminated aqueous media, the resulting aqueous suspension was equilibrated by stirring in dark for 60 min. After 60 min, stable aqueous suspension was irradiated with UV radiations ($\lambda = 200$ – 400 nm) for 80 min in home made 36 W photoreactor. During the irradiation process, after every 10 min absorbance spectra of the aqueous suspension was recorded to calculate the remnant dye concentration.

Room temperature energy resolved photoluminescence spectra were recorded using Fluoro Max-3 (Jobin–Yvon, Edison, NJ, USA) spectrofluorometer.

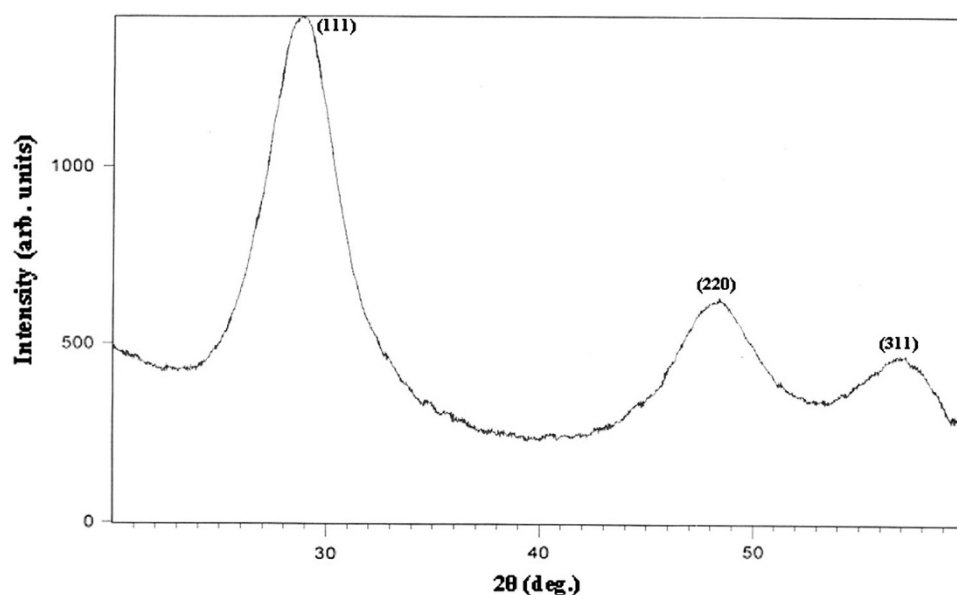
Results and discussion

All the recorded XRD patterns show peak broadening due to nano size formation, and one such X-ray diffractogram recorded for $\text{Zn}_{1-x}\text{Co}_x\text{S}$ is shown in Fig. 1. Comparison of the recorded XRD patterns with the standard JCPDS data base shows that the synthesized nanocrystals have zinc blende crystal structure. The average crystallite size calculated from recorded diffractograms using Scherrer formula (Cullity (1978)) was about 3 nm.

Figure 2 shows the TEM image recorded for $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals. Recorded micrograph shows the homogeneous morphology. The average particle size calculated from the TEM was about 3 nm, which is same as the average crystallite calculated from XRD. So, comparison of XRD and TEM results shows that the synthesized nanoparticles are single nanocrystals.

Figure 3 shows the room temperature energy resolved luminescence spectra of $\text{Zn}_{1-x}\text{Co}_x$ nanocrystals under

Fig. 1 XRD pattern of $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals



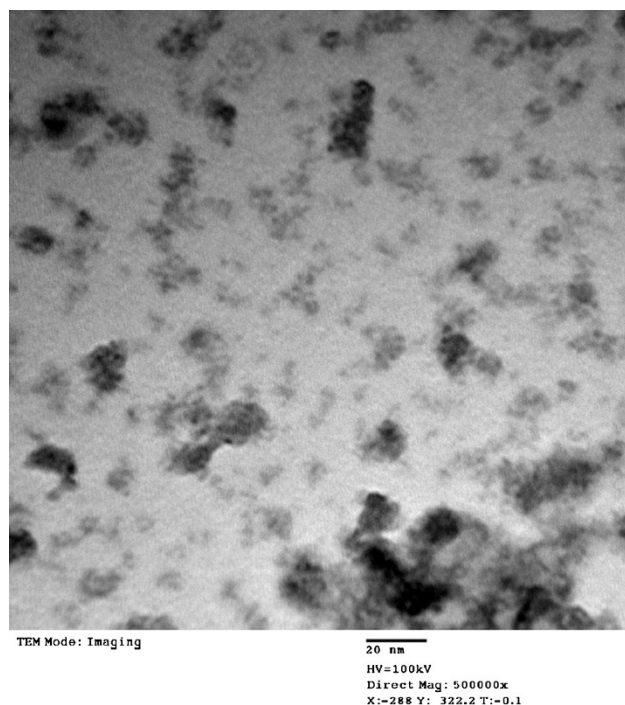


Fig. 2 TEM micrograph of $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals

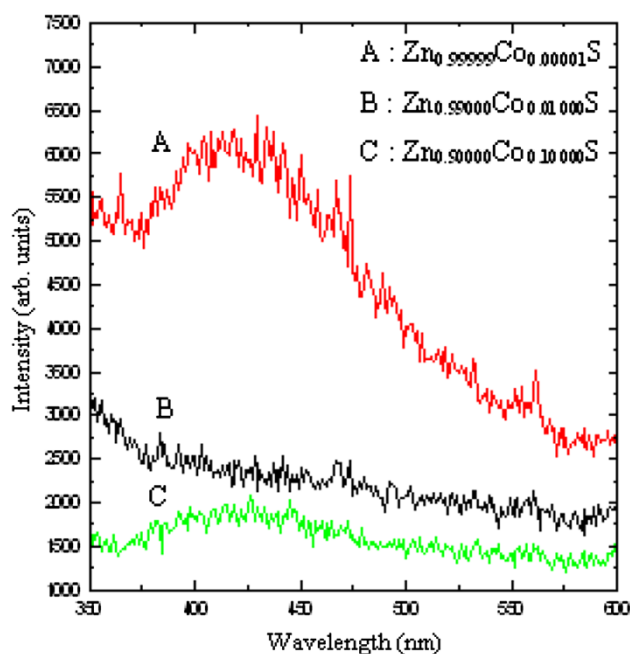


Fig. 3 Energy resolved photoluminescence spectra of $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals

325 nm excitation. It can be clearly seen from Fig. 3 that the spectrum A recorded for $\text{Zn}_{0.99999}\text{Co}_{0.00001}\text{S}$ nanocrystals shows broad emission peak centered at 429 nm, which is assigned to the radiative transition of electrons from shallow trap-states to sulfur vacancies, but the spectra B and C recorded, respectively, for $\text{Zn}_{0.99000}\text{Co}_{0.01000}\text{S}$ and

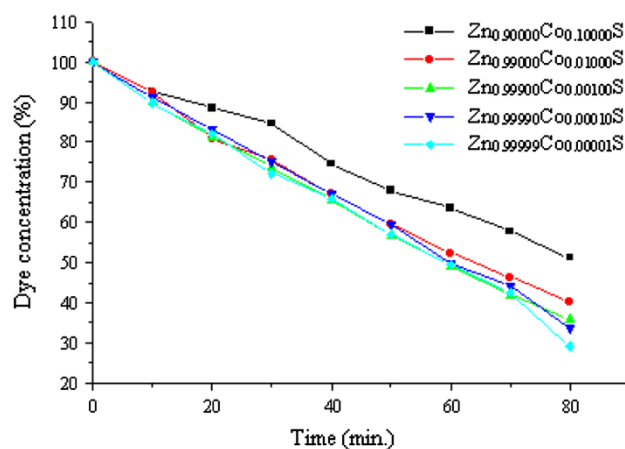


Fig. 4 Photo-degradation of MB dye with $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals

$\text{Zn}_{0.90000}\text{Co}_{0.10000}\text{S}$ nanocrystals show luminescence quenching. Co^{2+} ions are doped in ZnS lattice as substitutional impurity, the excited charge carriers trapped at these dopant trap-states relax non-radiatively instead of the radiative recombinations because Co^{2+} ions introduce ladder-like levels in the forbidden energy gap of the host lattice. At higher concentrations of the quencher impurity, the probability of charge carrier trapping at quencher states increases in comparison to direct host-related radiative transitions; this is the reason that luminescence completely quenched at higher dopant concentrations.

Figure 4 shows the photo-degradation of MB dye with $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals. It is evident from Fig. 4 that the remnant dye concentration after 80 min UV irradiation is having minimum value about 29 % in case of $\text{Zn}_{0.90000}\text{Co}_{0.10000}\text{S}$ nano photo-catalyst and maximum value about 41 % in case of $\text{Zn}_{0.99999}\text{Co}_{0.00001}\text{S}$ nano photo-catalyst. Photo-catalytic activity of nanocrystals goes on increasing with increasing concentration of Co^{2+} ions in ZnS lattice. Enhanced photo-catalytic activity with increasing dopant concentration is due to the reason that the probability of interfacial charge transfer goes on escalating with increasing concentration of dopant ions because charge carrier trapping at defect states augments at higher Co^{2+} concentrations.

Comparison of photoluminescence and photo-catalytic activity results as shown in Figs. 3 and 4 reveals that the interfacial charge transfer dominates over the radiative recombination with increasing concentration of Co^{2+} ions.

Conclusions

Aqueous chemical co-precipitation method is an efficient synthesis technique to synthesize monodisperse zinc blende nanocrystals of $\text{Zn}_{1-x}\text{Co}_x\text{S}$ ($0.00001 \leq x \leq 0.1$) having average particle size about 3 nm. Co^{2+} ions act as

luminescence quencher in ZnS lattice, luminescence quantum yield goes on deteriorating with increasing concentration of dopant ions. But, on the other hand, photocatalytic activity enhances with increasing value of 'x' in $\text{Zn}_{1-x}\text{Co}_x\text{S}$ nanocrystals. Interfacial charge transfer dominates over the radiative recombination of excited charge carriers at higher concentration of Co^{2+} ions. The synthesized nanocrystals are good candidates for efficient water purification and environmental cleaning.

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